STRUCTURAL, ELECTRO-MAGNETIC AND ELECTRICAL ANALYSIS IN MONOVALENT DOPED $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ MANGANITES

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ABSTRACT

The polycrystalline $Nd_{0.75}Na_{0.25-x}K_xMn_1O_3$ (x = 0, 0.05 and 0.10) samples were prepared using solid state reaction method. K doped manganites have been investigated to study its effect on crystalline phase and surface morphology as well as electrical transport and magnetic properties. However most of study show inconsistent result regarding to the electrical transport and magnetic properties as well as crystalline phase and morphology study. Thus, further detailed study need to be conducted in order to explain the properties of manganites. The structured properties of the $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ manganite have been characterized using X-ray diffraction measurement showing the crystalline phase of samples were single phased and indexed as orthorhombic structure (*Pnma* space group). The morphological study from scanning electron microscope showed that there were improvements on the grains boundaries and sizes as well as the compactness with K doping. On the other hand, DC electrical resistivity measurement showed all samples exhibit insulating behavior. Analysis of $d\ln\rho/dT^{-1}$ vs. T revealed a peak at temperature 210K for x = 0 and the peaks were shifted to the lower temperature around 190 K and 165 K for x = 0.05 and x = 0.1 respectively. Meanwhile, the investigation on magnetic behavior showed all samples exhibit transition from paramagnetic phase to anti-ferromagnetic phase with decreasing temperature and the T_N was observed to shift to lower temperature. Apart from that, the electrical analysis; variable range hopping (VRH) model was selected in order to explain the electrical behavior of the samples as the value of R^2 is approached to 0.9999 as it has highest value compared to small polaron hoping (SPH) model. In conclusion, the effect of K^+ doped on $Nd_{0.75}Na_{0.25-x}K_xMn_1O_3$ were effected the properties of manganites including the structure, surface morphology, magnetic and electrical due to the different ionic radius and reduction in the distortion of MnO_6 octahedral.

ABSTRAK

Kaedah yang digunakan untuk menyediakan bahan campuran kristal $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ (x = 0, 0.05 dan 0.10) adalah kaedah reaksi keadaan pepejal. Campuran K kedalam manganites telah dilakukan untuk mengkaji kesan campuran pada fasa kristal dan permukaan morfologi serta ciri-ciri pengangkutan elektrik dan sifat magnetik manganites. Walau bagaimanapun, kebanyakan kajian tidak menunjukkan keputusan yang stabil berhubung ciri-ciri pengangkutan elektrik dan sifat magnetic, begitu juga dengan fasa kristal dan permukaan morfologi. Justeru, kajian yang menyeluruh harus dilakukan untuk menerangkan ciri-ciri maganite ini. Sifat-sifat struktur kompenan $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ telah dicirikan dengan menggunakan pengukuran pembelauan sinaran-X (XRD) dan terbukti bahawa fasa kristal sampel pada dasarnya bertahap tulen dan struktur adalah berbentuk orthorhombik (kumpulan kelas *Pnma*). Kajian morfologi permukaan dari Microskop electron pengimbasan menunjukkan terdapat peningkatan pada sempadan butir dan saiz serta kekompakan dengan peningkatan K. Sebaliknya, pengukuran kerintangan elektrik arus terus menunjukkan semua sampel bersifat penebat. Analisis $d\ln\rho / dT^{-1}$ vs T menunjukkan wujudnya puncak yang jelas dan dapat dilihat pada suhu 210K untuk x = 0 dan menurun ke suhu lebih rendah sekitar 190 K (x = 0.05) dan 165 K (x = 0.1). Sementara itu, kajian terhadap sifat magnet menunjukkan berlakunya peralihan fasa dari fasa paramagnetik kepada fasa anti-ferromagnetik dengan suhu berkurangan untuk semua sampel, dan T_N beralih kepada suhu yang lebih rendah. Di samping itu, analisis data elektrik, *variable range hopping* (VRH) telah dipilih untuk menjelaskan ciri-ciri elektrik pada sampel kerana nilai R^2 lebih menghampiri nilai 0.9999 berbanding *small polaran hoping* (SPH). Oleh itu, kesan daripada K doping didalam campuran $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ mempengaruhi ciri ciri manganites termasuk fasa kristal dan permukaan morfologi serta ciri-ciri pengangkutan elektrik dan sifat magnetik disebabkan pengurangan penyimpangan MnO_6 oktahedral.

CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

ρ	Resistivity
χ'	Susceptibility
ABX_3	Perovskite chemical formula
ACS	AC susceptibility
AFM	Antiferromagnetic
A_C	The sum of atomic weight of all cation in the formula unit
A_A	The sum of the atomic weight of all anions in the formula unit
Abc	Lattice parameter
Ba	Barium
CMR	Colossal magneto-resistance
Co	Cobalt
Co^{3+}	Cobalt (III) ion
CO	Charge-order
CO_2	Carbon dioxide
Cr	Chromium
D	Density
D_x	Powder density
DE	Double-exchange
FMM	Ferromagnetic metallic
h k l	Miller indices
JT	Jahn-Teller
K^+	Potassium ion
K_2Co_3	Potassium carbonate
Li^+	Lithium ion
Mn^{3+}	Magnesium (III) ion
Mn^{4+}	Magnesium (IV) ion
MnO_2	Manganese (IV) oxide
MnO_6	Manganese oxide octahedral

MI	Metal-insulator
n’	The number of formula units within the unit cell
Na^{+}	Sodium ion
Na_2Co_3	Sodium carbonate
Nd	Neodynium
Ni	Nickel
Nd_2O_3	Neodymium (III) oxide
O^{2-}	Oxide ion
PMI	Paramagnetic insulating
PM	Paramagnetic
$<r_A>$	Average ionic radius
Sr^{2+}	Strontium ion
SEM	Scanning electron microscope
SPH	Small polaron hopping
T	Temperature
T_C	Curie temperature
T_{CO}	Charge-order temperature
T_{MI}	Metal-insulator transition
T_N	Neel temperature
VRH	Variable range hopping
V	Unit cell volume
W_{air}	Weight in air
$W_{acetone}$	Weight in acetone
XRD	X-ray diffraction

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1. Razali, S. A., Ibrahim, N., Shamsuddin, S., & Noh, M. Z. (2018). Observation of charge ordering signal in monovalent doped $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ ($0 \leq x \leq 0.10$) manganites. International Journal of Engineering & Technology, 7(4.30)85-88.
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2. Mannan, N. N., Razali, S. A., Shamsuddin, S., Noh, M. Z., & Mohamed, Z. (2018). Effect of Co^{3+} substitution on electro-mangnetic properties of $Pr_{0.75}Na_{0.25}MnO_3$ and $Nd_{0.75}Na_{0.25}MnO_3$ managnites. International Journal of Engineering & Technology, 7(4.30)389-392.
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3. Mannan, N. N., Razali, S. A., Shamsuddin, S., & Noh, M. Z. (2017). Crystalline phase, surface morphology and electrical properties of monovalent-doped $Nd_{0.75}Na_{0.25}Mn_{x-1}Co_xO_3$. Journal of Science & Technology, Vol. 9 No. 3 65-69.

CHAPTER 1

INTRODUCTION

1.1 Background of study

In the last decade, extensive research has been carried out toward the understanding of the extraordinary structural, magnetic, electrical and thermal transport properties of doped perovskite-type manganites with general formula $R_{1-x}A_xMnO_3$ (where R is rare earth metal and A is monovalent/divalent alkali metal). The interest is based on fundamental physics and chemistry due to their high chemical stability, sample preparation methods, doping dependence of their magnetic transition temperature (Zhang *et al.*, 2013), potential application in electronic devices (Phan *et al*., 2014, Gdaiem *et.al*, 2016) and the complex magneto-electrical as well as colossal magneto-resistance (CMR) properties (Shamsuddin *et al*., 2013; Malik *et al*., 2014, Pollert *et. al*, 2004).

The percentage amount of divalent and monovalent cation ions, size of ionic radii are said to have a great influence on the magnetic and transport properties of perovskite material (Akyol *et al*., 2017). Several reports showed that substitution of a small amount of transition metal element at Mn-site can influence the magnetic and electrical transport properties of manganite compound. However, elemental substitution at A-site also gives extensive impact on the properties of the manganites compound due to the changing of electron bandwidth and the size mismatch, controlled by A-site cation average size (Koubaa *et al*., 2009). On top of that, it was mentioned the relationship between magnetic and transport properties of this oxides can be well elucidated by using the mechanism of double exchange (DE) of the Mn^{3+}

and Mn^{4+}. On the other hand, observation of surface morphology studies in manganites has been suggested as a successful tool in providing valuable information such as grain size and grain boundaries as well as porosity, which can help to show the interaction between morphological and structural study.

The electrical analysis also plays an important role in providing a better understating the variation of electrical resistivity in the material (Masroor *et al*., 2016) that describe the electron scattering model and hopping model for metallic and insulating part respectively. To further understand the variation of resistivity behavior in monovalent/divalent doped manganites at the metallic region with zero magnetic field applied, the resistivity data was fitted using a theoretical model. Research proved that resistivity behavior in some manganites is due to combination of weak electron localization and some scattering mechanisms, such as electron-electron, electron-magnon and electron-phonon scattering processes in ferromagnetic phase (Ibrahim *et al*., 2010). The phase transition of ferromagnetic-paramagnetic with the increased of dopant content occurs when the charge ordered state was weakened. The measurement of the electrical resistivity at low temperature showed the increase in tolerance factor in which indicates the reduction in MnO_6 distortion while enhancing the interaction of DE. Alternatively, in order to understand clearly the electrical analysis at the insulating region, the resistivity data are fitted using two different hopping models, namely, variable range hopping (VRH) and small polaron hopping (SPH). VRH models describe the electrical analysis in manganite based on doping-induced disorder caused by the random distribution of defects, while SPH model implies the existence of strong electron-phonon coupling caused by the Jahn-Teller lattice distortion (Rozilah *et al*., 2017).

As for that, manganites are manganese oxides material that has their own specialties behavior and one of convenient magnetic ceramic material working at low temperature. Properties of manganites can be altered by some factors, and this study focus on doping factor. Currently, researchers had studied the effect of doping agent on the magnetic and electrical transport of perovksite-manganites structure. Previous study has investigated the effect of Chromium (Cr) doping at Mn-site manganites on the charge-order (CO) state, magnetic and electrical properties of $Nd_{0.75}Na_{0.25}MnO_3$ manganites (Zhang *et al.,* 2011). However, the study on the effect of monovalent doped manganites at A-site to charge ordering is still limited. Hence, as a

consequence, this study reports on the DC electrical resistivity and AC susceptibility measurement on $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ ($0 \leq x \leq 0.10$) manganite with the aim to investigate the effect of partial K-doped on electrical transport and magnetic properties as well as provide an understanding of CO in the material. Results from X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurement as well as values of density and porosity are also presented and discussed.

1.2 Problem statement

Among rare earth element family, Nd based manganites, $Nd_{0.75}Na_{0.25}MnO_3$, has caught attention as it displays the existence of charge ordered at T_{CO} at the area below 170 K (Nabilah *et al*., 2017; Tang *et al*., 2008). Attractively, by substituting a small amount of charged ions at A/B-site, the properties of a material will be altered. For instance, study on $La_{0.7}Nd_xBa_{(0.3-x)}MnO_3$ showed particles are not fully-densified which would be attributed to the large atomic radius and consequently the high activation energy of Ba atom for the parent compound, but Nd substitution at A-site causes a significant decrease in the grain size (Gokhan Unlu *et al*., 2016). Besides that, Maryam *et al*., 2018 revealed that the parent compound of $Nd_{0.75}Na_{0.25}MnO_3$ exhibited insulating behavior. Then, when small amount of Ni was substituted at Mn-site, it was induced to metallic behavior suggesting by weakened of CO state and enhancement double-exchange (DE) mechanism. As stated by Li *et al.*, 2004, the interaction of double exchange on perovskite-base manganites doped with monovalent alkali earth metal cation ions is much stronger compared to divalent alkali earth metal. In the last past decade, there were a few pioneer work conducted on mixed-valent manganite doped with monovalent cation ions such as Na^+, K^+ and Li^+. Lanthanum-based manganites doped with Potassium (K), $La_{0.7}Sr_{0.3-x}K_xMnO_3$, make a transition from paramagnetic to ferromagnetic transition at low temperature and thus show that potassium doping decrease Curie temperature, T_c and lead to DE interactions (Koubaa *et al.*, 2009). Besides, based on Rozilah *et al*., 2017, AC susceptibility measurement for parent compound of $Pr_{0.75}Na_{0.25-x}K_xMnO_3$ manganite showed a paramagnetic behavior, then initially weakened CO when a small amount of K^+ (x =0.05-0.10) was doped. By further increasing up to x = 0.15-0.20, the CO state was successfully suppressed and inducing ferromagnetic-paramagnetic

transition with Curie temperature, *Tc* increased with *x* content. For electrical resistivity measurement, $x = 0$ sample exhibit as insulating behavior, then by increasing amount of K^+, samples showed metal-insulator transition as transition temperature, T_{MI} increased suggested due to the enhancement of double exchange interaction. However, most of the substitution does not show full suppression of CO-AFM phases probably due to dopant level. As such, the influence of magnetics ions on host composition need to be further investigated to understand the role of the magnetic ions in the CO phase. Hence, magnetic and electrical resistivity properties measured at low temperature would be very interesting to study as this could reveal the information of CO state in the sample as well as provide a better understanding on the properties when other element was substitute at A-site of the compound. In addition, analyze of the electrical resistivity data will give a better understanding of the hopping process in this compound.

1.3 Objectives of study

The objectives of this research are:

i. To determine the structure and surface morphology of $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ by using powder X-ray diffraction (XRD) and scanning electron microscope (SEM) measurement respectively.

ii. To investigate the influence of K-doped on magnetic and electrical transport properties of $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ at a lower temperature using AC susceptibility (ACS) and DC electrical resistivity measurement respectively.

iii. To explain the electrical behavior of $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ manganites using variable range hopping (VRH) and small polaran hopping (SPH).

1.4 Scope of study

This study covers the roles of monovalent cations ion, Potassium (K^+) doped on $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ manganites which have been synthesized by using conventional solid state reaction method. This method involves the process of mixing, grinding, calcined, pelleting and sintering in order to complete the preparation process. The crystalline phase of the manganite compound was carried out at room temperature using X-ray diffraction (XRD) measurement. Observation of the surface morphology was obtained by scanning electron microscope (SEM) measurement at room temperature. The magnetic measurement was analyzed using AC susceptometer with the temperature at range 50K to 300K. Electrical transport properties were performed at a temperature range of 50K - 300K using a DC electrical resistivity measurement utilized using the four-point-probe method. For further understanding, analysis of electrical analysis also carried out using the VRH and SPH model to propose suitable model in explaining the electrical resistivity data.

1.5 Significance of study

Rare-earth manganites perovskite structure are very special due to their interesting physical and magnetic properties. It is capable to dope with other elements to change their properties as well as increasing performance toward the application of magnetic sensor, communication and transportation. By doping process such as K^+ on $La_{0.8}Cd_{0.2-x}K_xMnO_3$ manganite it showed increasing of electrical properties and enhancement of magnetic properties by shifting the transition temperature of T_{MI} and T_C (Dhahri *et al*,. 2010). This study is important as the substitution of Potassium (K) ion at A-site for $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ sample will reveal the influence of the substitution on the structure, magnetic and transport properties. Generally, small amount substitution of a monovalent or divalent ion at A-site of rare-earth manganites will influence the physical properties of the materials, thus substitution of alkaline ions in this Nd-based significantly induced the magnetic properties from ferromagnetic to paramagnetic phase and the electrical properties which are metal–insulator (MI) transition at low temperature measurement. This phenomenon occurred suggestively due to the presence of charge-ordered phase which closely

related to the size of the ionic radius doping agent that affected the average size of A-site cation, electron-bandwidth and the Mn-O-Mn bond angle. This study also important to describe the mechanism in $Nd_{0.75}Na_{0.25}MnO_3$ manganites. In addition, this study also provided additional information and knowledge about CO by providing the information related to the mechanism and properties of manganites. Apart from that, it also provides additional knowledge about the electrical properties by proposing a suitable model in explaining the electrical data where the electrical resistivity data were fitted using the VRH and SPH model.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this research study, perovskite-type manganite ($R_{1-x}A_xMnO_3$) is used as the main compound where R is a trivalent ion that includes (La^{3+}, Pr^{3+}, Nd^{3+}). Meanwhile, A stand for ion from group one (monovalent ion) or group two (divalent ion) which include of (Ag^+, Na^+, Li^+) and (Ca^{2+}, Sr^{2+}, Ba^{2+}) respectively. Rozilah *et al.*, 2017 in the research study, state that perovskite-type manganites possess its own unique properties such as structure transformation, metal-insulator (MI), charge ordering (CO), and Colossal Magnetoresistance (CMR). All the properties come from the interaction between two ions which are Mn^{3+} and Mn^{4+}. The interaction of Double Exchange (DE) between those two ions will generate ferromagnetic metallic (FMM) state while Jahn-Teller will provide paramagnetic metal insulator (PMI) transition.

In this research study, the monovalent element which is potassium was used to dope with the parent compound of $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ to see if there are any transition of ferromagnetic-paramagnetic transition or metal-insulator phenomenon. The previous study stated that the monovalent elements are commonly known as the function to convert twice more Mn^{3+} to Mn^{4+} ion compared to divalent elements (Thaljaoui *et al.*, 2014a; Thaljaoui *et al.*, 2014b). Many previous studies was reported about the influence of potassium doped manganite on the structural and electrical properties. Rozilah *et al.*, 2017 in the previous study stated that with the substitution of the potassium (x = 0, 0.05, 0.10, 0.15) has weakened the CO state

and actuated the ferromagnetic-paramagnetic transition above Curie temperature T_C. This statement is also supported by Thaljaoui *et al.,* 2014b, saying an increase in potassium substitution content a shift paramagnetic to the ferromagnetic transition temperature is showed. The substitution of potassium increase the unit cell volume of a compound. Moreover, Koubaa *et al.,* 2009a and Koubaa *et al.,* 2009b state that the unit cell volume of the samples was increase when there is an increase in the potassium content. As stated before, the increase in quantity of potassium doped induce a sharp transition from paramagnetic to ferromagnetic and at the same time this substitution leads to a decrease in the Curie temperature, T_C. In simple word, based on the previous study the magnetic measurement observed on the potassium doped manganites have been exhibits a transition from paramagnetic to ferromagnetic with decreasing temperature.

From previous study of $La_{0.7}Sr_{0.3-x}Na_xMnO_3$ doped with Na, electrical investigation shows that the sample exhibit semiconducting behavior at high temperature while at low temperature it behave metallic-like. Besides, according to Koubaa *et al.,* 2009b, when monovalent element use as the dopant agent, it lead to the increase of Mn^{4+} and the double exchange interaction between Mn−O−Mn angle became weakened. Another way to alter the properties is by doping other transition metal ions on the Mn-site (B-site). As stated by Nabilah *et al.,* 2017 the action of doping Co element at Mn-site of the $Nd_{0.75}Na_{0.25}MnO_3$ modified the properties and give beneficial information of charge-ordered (CO) state. The result from the electrical transport properties analyze by the four-point-probe method, it shows that all the samples (y = 0 – 0.05) display insulating behavior in the temperature range of 80 K – 300 K. All the resistivity slope of insulating samples show a minimal change at the temperature of 200K. It also stated that the localization peak of analyzation $d\ln\rho/dT^{-1}$ occcured within charge ordering transition from low to higher temperature. For certain condition, manganites can reveal metallic characteristic by applying a high magnetic field and it has been suppressed the charge-ordered state (Li *et al.,* 2006). As for half-doped $Pr_{0.5}Ca_{0.5}MnO_3$ with doping element such as Mg^{2+}, Al^{3+}, Fe^{3+}, Ti^{4+} and Sn^{4+} it was shown to remain as insulating compound until there is an applied magnetic field of 7 T. A metal-insulator transition. This occur due to the compound having magnetic

field result in the to weakening of CO state, which is contrast to the parent compound of $Pr_{0.5}Ca_{0.5}MnO_3$ (Raveau *et al*., 1997)

2.2 Structure of ceramic

2.2.1 Crystal structure

The crystal structures for those ceramic materials that have predominantly ionic atomic bondings are being composed of electrically charged ions instead of atoms. It involves all the ions that consist in that material which is positively charged metallic ions (cations) that give up their valence electrons to the nonmetallic ion (anions) that carried negative charged. The crystal structure can be influenced by two different characteristics of the component ions in crystalline ceramic materials. The first characteristic which is the magnitude of the electrical charge on each of the component ions, it means that the crystal must be electrically neutral. All the ions have to complement each other to achieve this charge balance for both cation positive charged and anion negatively charged. The second criterion involves the relative sizes of the cations and anions. Basically, cations are ordinarily smaller that anions and consequently the ratio is less than unity because the metallic elements give up electrons when ionized. Each cation prefers to have as many nearest-neighbor anions as possible, same goes to anions that also desire a maximum number of cation nearest neighbors. At the end of this, the stability can be explained by a crystal lattice of material. These ceramic crystal structures become stable when the surrounding of anions all in contact with that cations as illustrated in Figure 2.1.

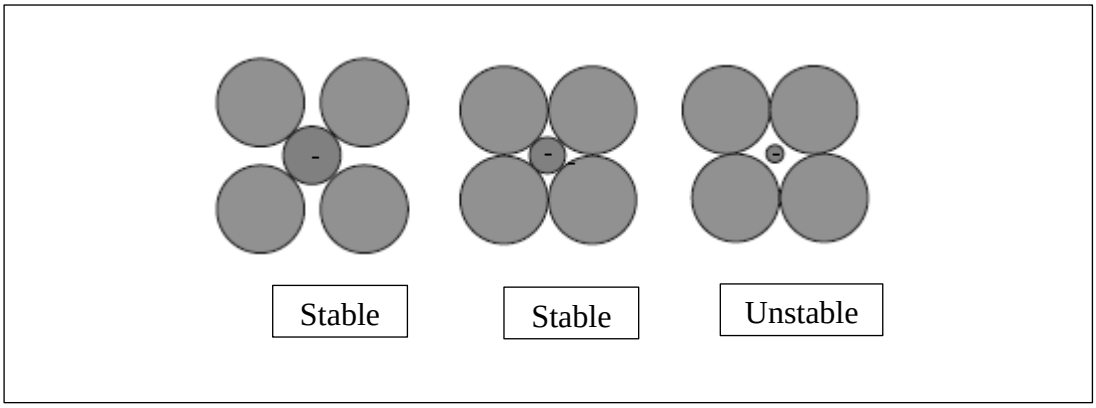

Figure 2.1: Stable and unstable anion–cation coordination configurations.

2.2.2 Crystal lattice

The concept of crystal lattice was an interpretation of the diffraction pattern of the regular atomic array which pioneered by Lawrence and William Bragg. The position of atoms in the crystal must be at a fixed distance from one another. The interatomic separation constituted an array of lattice vectors defined as the elementary unit cell of volume. These parameters are displayed the symmetry elements in bulk crystal.

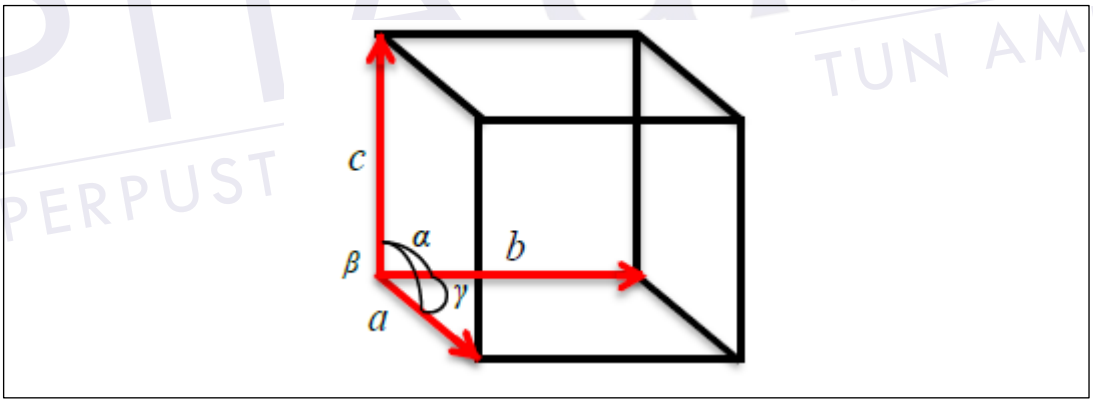

Figure 2.2: Schematic representation lattice parameters of a cubic unit cell (Brandon & Kaplan. 2001)

Lattice defined as a set of periodic points in space. (*a*,*b*,*c*) are the three coordinates length indicated by placing the origin at lattice points. The angles are (*α, β, γ*) subtended by lattice axes illustrated in Figure 2.2. Seven crystal systems are generated from the different values of (*a, b, c*) and (*α, β, γ*) namely triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal and cubic (Frank. 2009, Brandon & Kaplan. 2001). The structure of crystalline materials could be confirmed using powder X-ray diffraction technique. The analysis conducted

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